

a pressure-temperature diagram as shown in Fig.2. When the product was a mixture of the two phases, their relative quantity was estimated from the intensities of powder diffraction peaks. From the figure, the equilibrium phase boundary can be expressed in terms of the equation; $P(\text{kbar})=26.7+0.0265T(^{\circ}\text{C})$.

Considerations: The pressure induced phase transition of ABO₄ compounds has been examined by several researchers(7,8,9,10). Among them, Nicol and Durana(1) claimed through their high pressure Raman spectra measurements that CaWO₄ and CaMoO₄ transformed reversibly to a high pressure form at about 20kbars which was of similar structure to wolframite. On the other hand, Sleight(2) showed that the quenched specimens of CaWO₄, CdWO₄, CaMoO₄ and CdMoO₄ did not reveal any high pressure form. It was therefore considered that these wolframite-like high pressure phases are not quenchable. In comparison with those observations, it is interesting to note that the high pressure forms are obtained in quenched products for PbWO₄(3) and BaWO₄ where the A-cations are relatively large. As Fig.2 shows, the dP/dT is positive in the transformation of BaWO₄-I to BaWO₄-II. This is similar to the behaviors of the high pressure form of PbWO₄.

In the BaWO₄-I → BaWO₄-II transformation, the volume of the unit cell decreases by 12.1% of the I-form(the cell volume of the II-form is normalized to a four formula unit cell). If the transformation is of a scheelite → wolframite structure, no change in the average coordination number may result in much smaller volume decrease. Shannon and Prewitt(11) discussed an empirical tendency that a larger decrease of cell volume is associated with an increase of coordination number. In fact, the present case, the decrease amounting to 12.1% is associated with an increase in the average coordination number in the high pressure phase.

Acknowledgements

We are very grateful to Dr. I.Kawada of this Institute, for X-ray analysis suggestions. We also indebted to Mr. H. Ohashi and Mr. M.Saeki for their helpful comments.

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